ALD of Manganese Silicate

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Outline

Potential Applications of Manganese Silicate

ALD Process for Manganese Oxide, MnO

ALD Process for Manganese Silicate

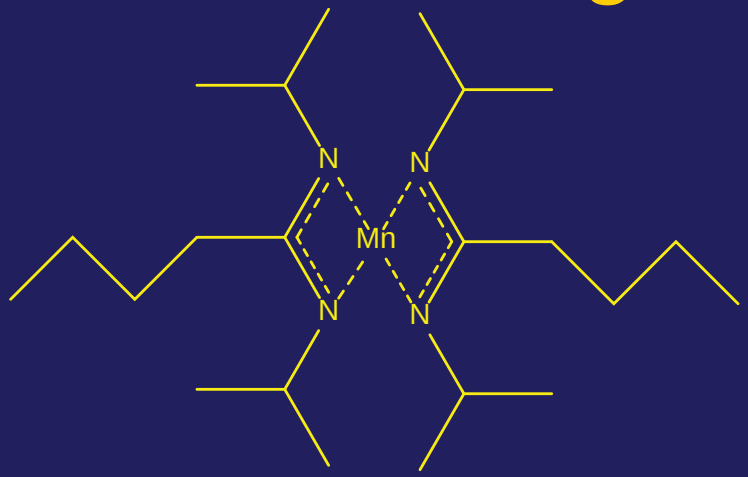
Properties of Manganese Silicate

Potential Applications of $MnSi_xO_y$

Copper wires in computer chips could use $MnSi_xO_y$ as a

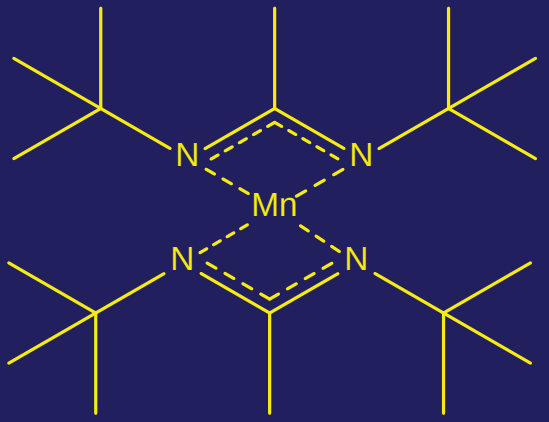
- barrier to diffusion of copper, water and oxygen
- adhesion promoter between copper and insulators
- nucleating layer for vapor deposition of copper

Manganese Precursors



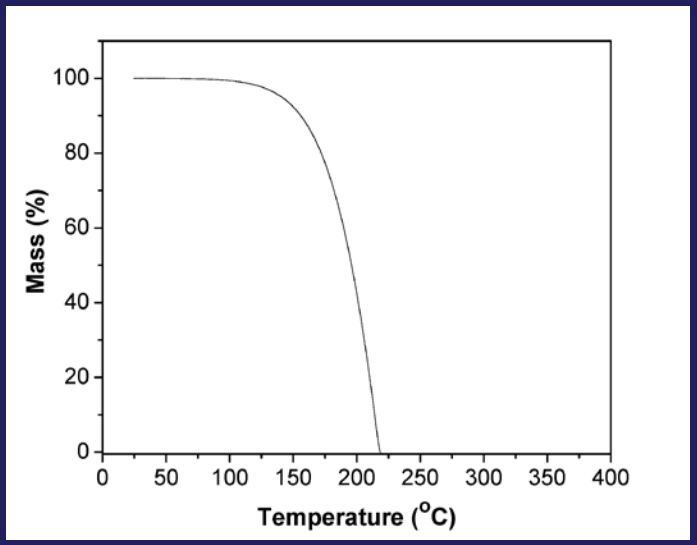
manganese(II)
bis(*N,N'*-diisopropylpentamidinate)

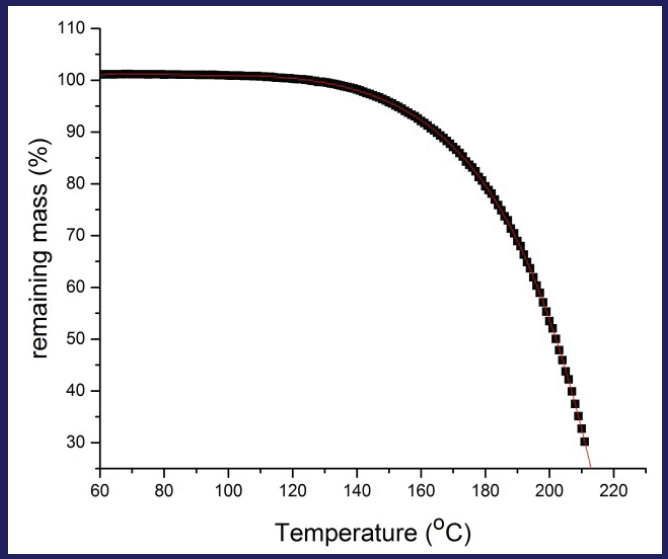
melting point: 60 °C
boiling point: 120 °C / 0.02 torr



manganese(II)
bis(*N,N'*-di-*tert*-butylacetamidinate)

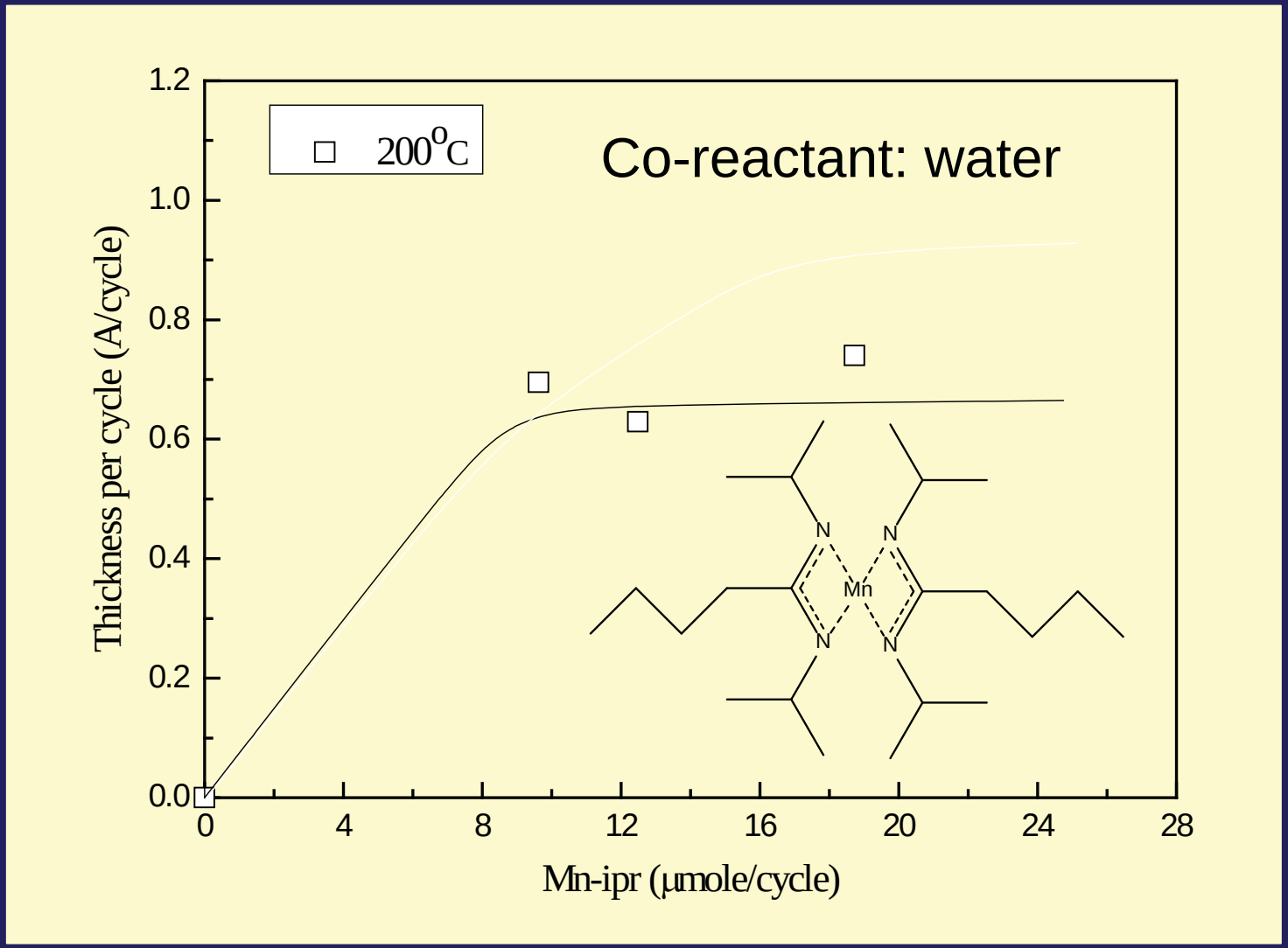
melting point: 107 °C
boiling point: 100 °C/ 0.07 torr





Saturation Curve for Manganese Oxide

Saturated for doses > 10^{-5} moles/cycle



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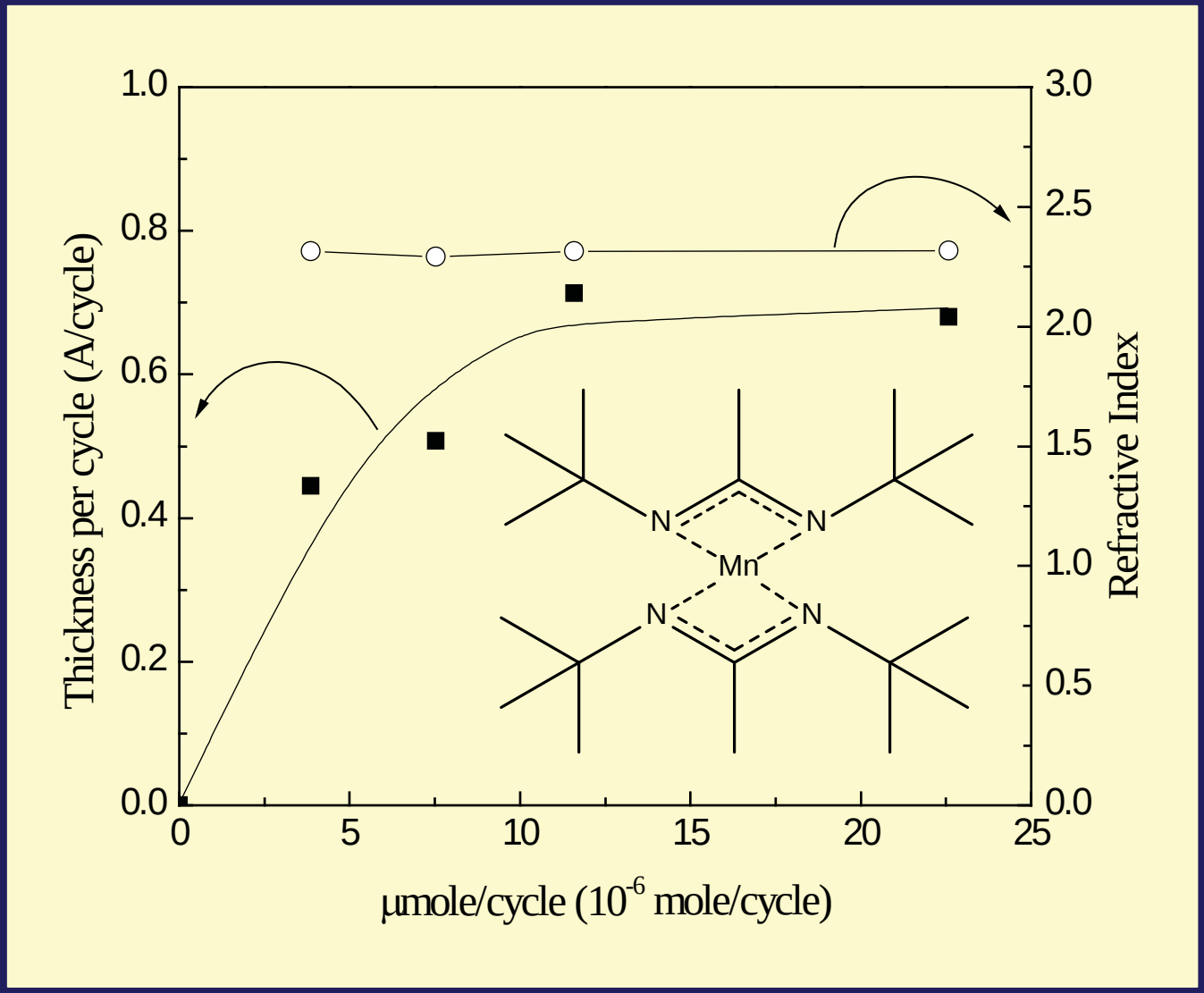
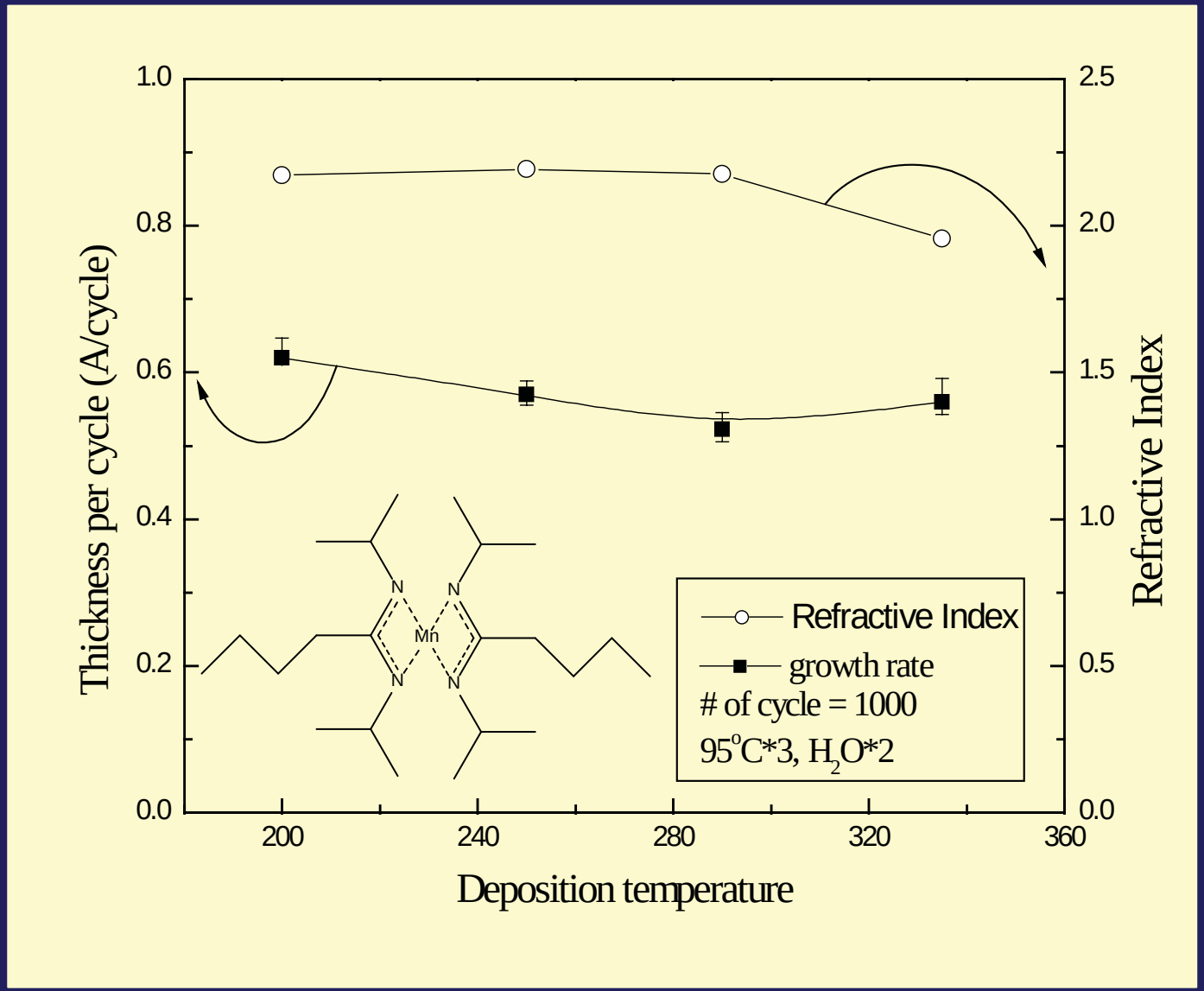


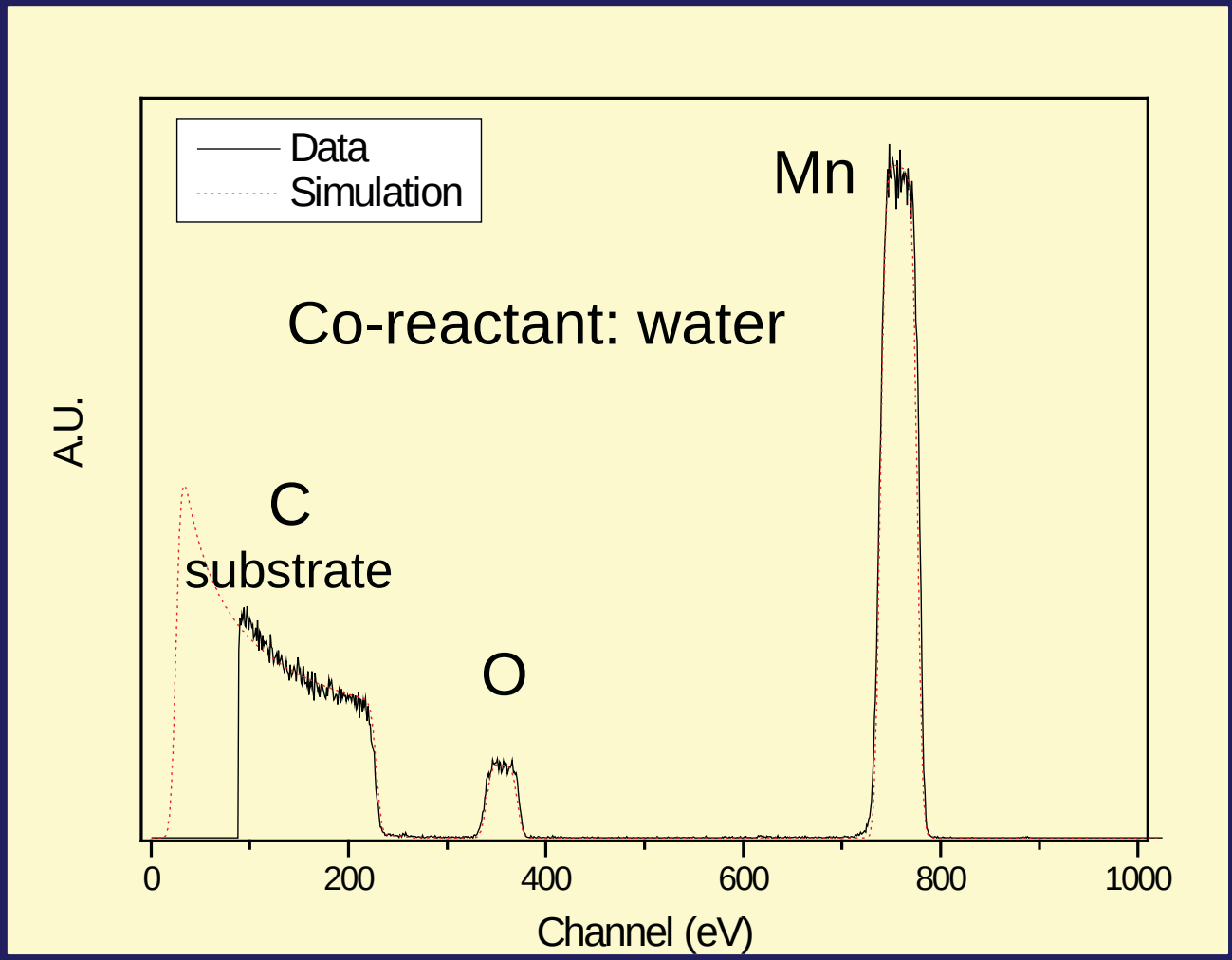
Thickness per Cycle for Manganese Oxide

nearly constant from 200 to 340 ºC



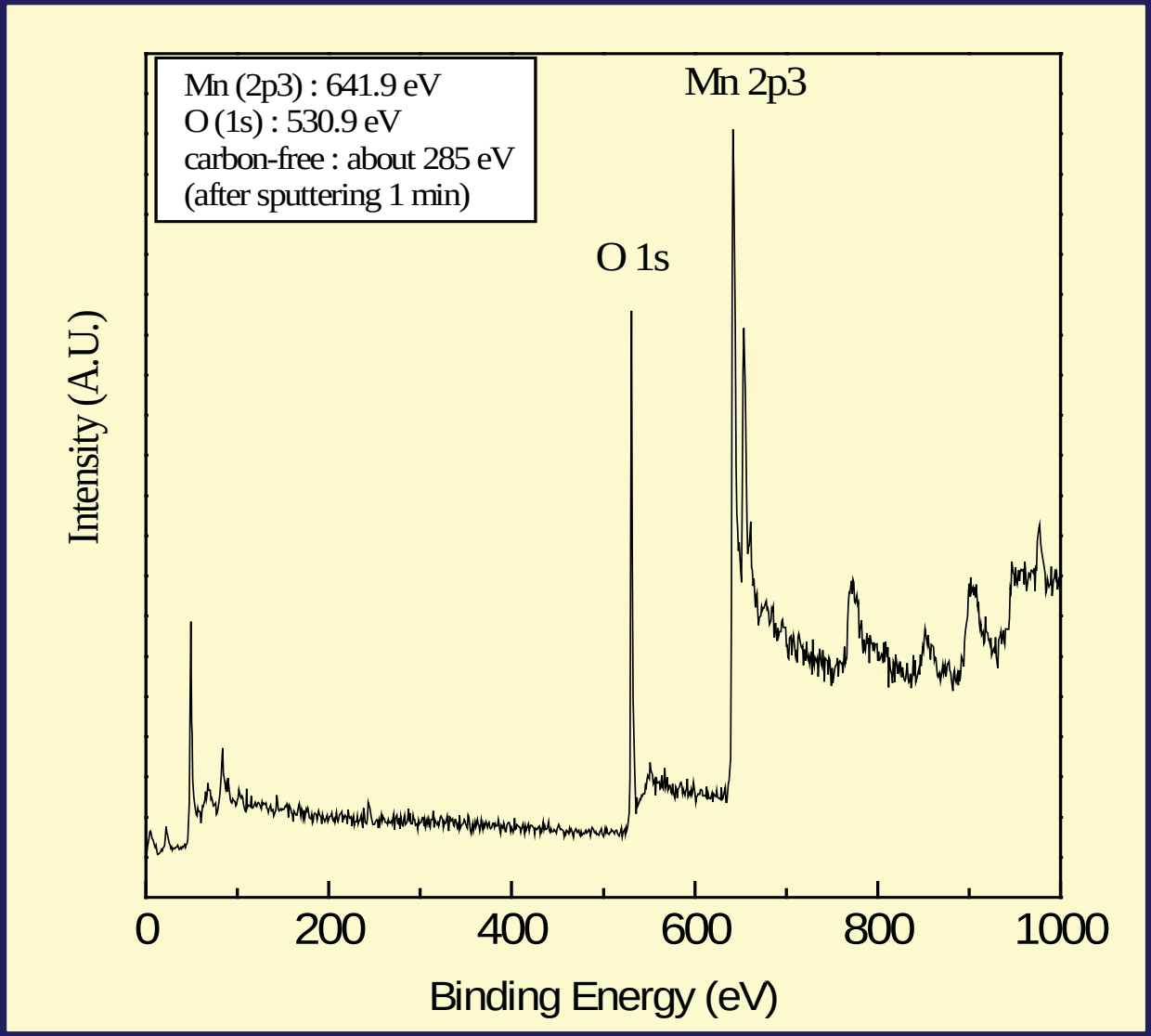
Rutherford Backscattering Spectroscopy

=> Stoichiometry MnO Adding O_2 cycles => MnO_2

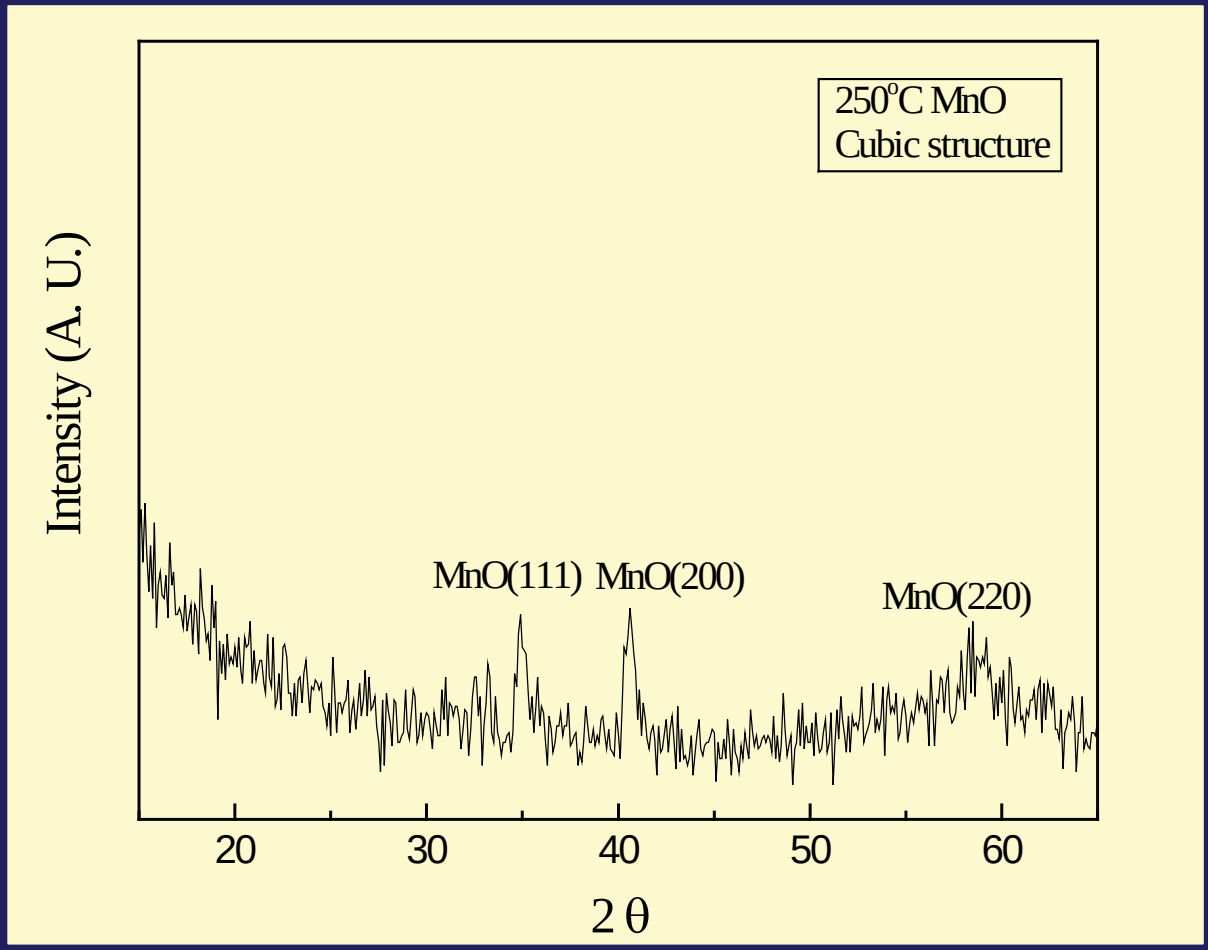


X-Ray Photoelectron Spectroscopy

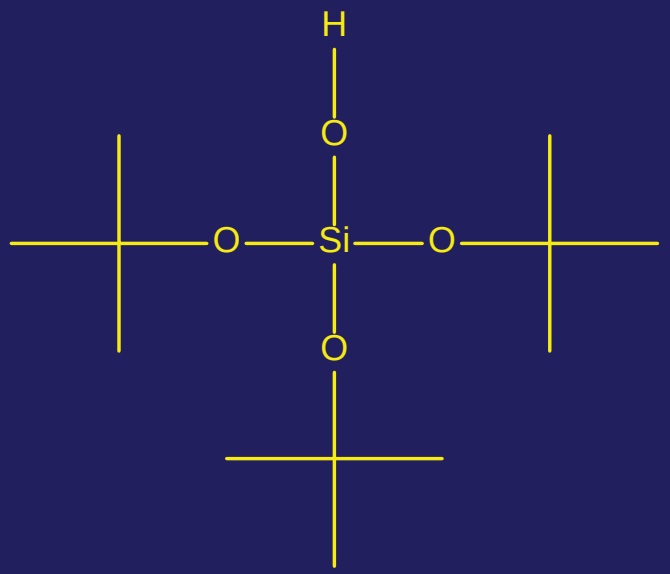
< 1% C or N impurities



XRD shows polycrystalline MnO

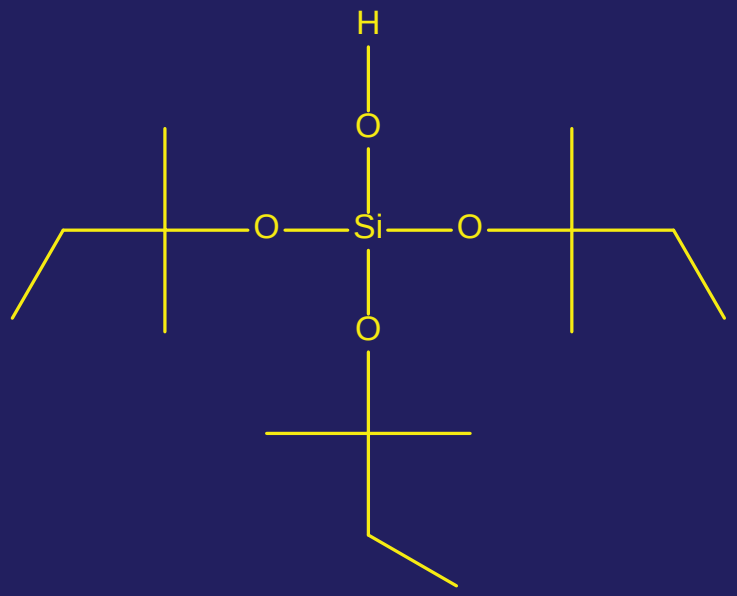


Precursors for Silicon and Oxygen



tris-*tert*-butoxysilanol (TBS)

melting point: 63 - 65 °C
boiling point: 205 - 210 °C/ 760 torr



tris-*tert*-pentoxysilanol (TPS)

melting point: < 20 °C
boiling point: 96-99 °C/ 2-3 torr

ALD Conditions for Manganese Silicate

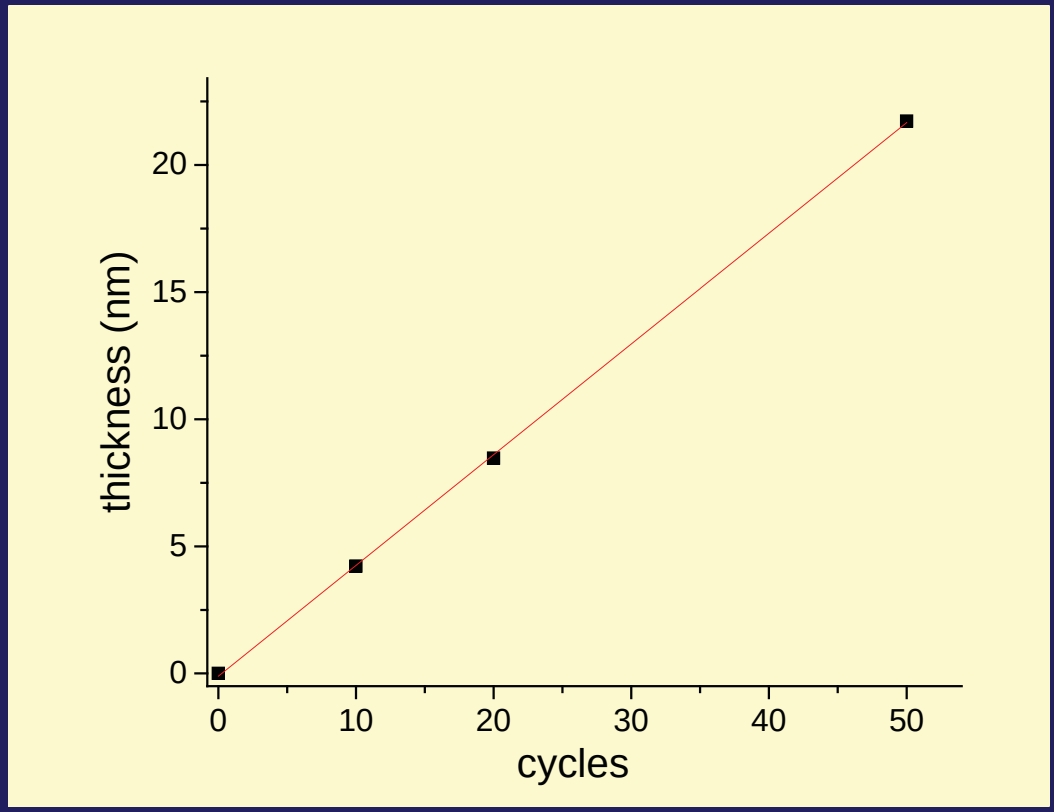
Substrate: SiO_2/Si
UV ozone cleaning: 2 min
Drying at 350°C: 1 hour

Mn amidinate source =105°C
Si/O source (TPS)=120°C

T(substrate)= 350°C

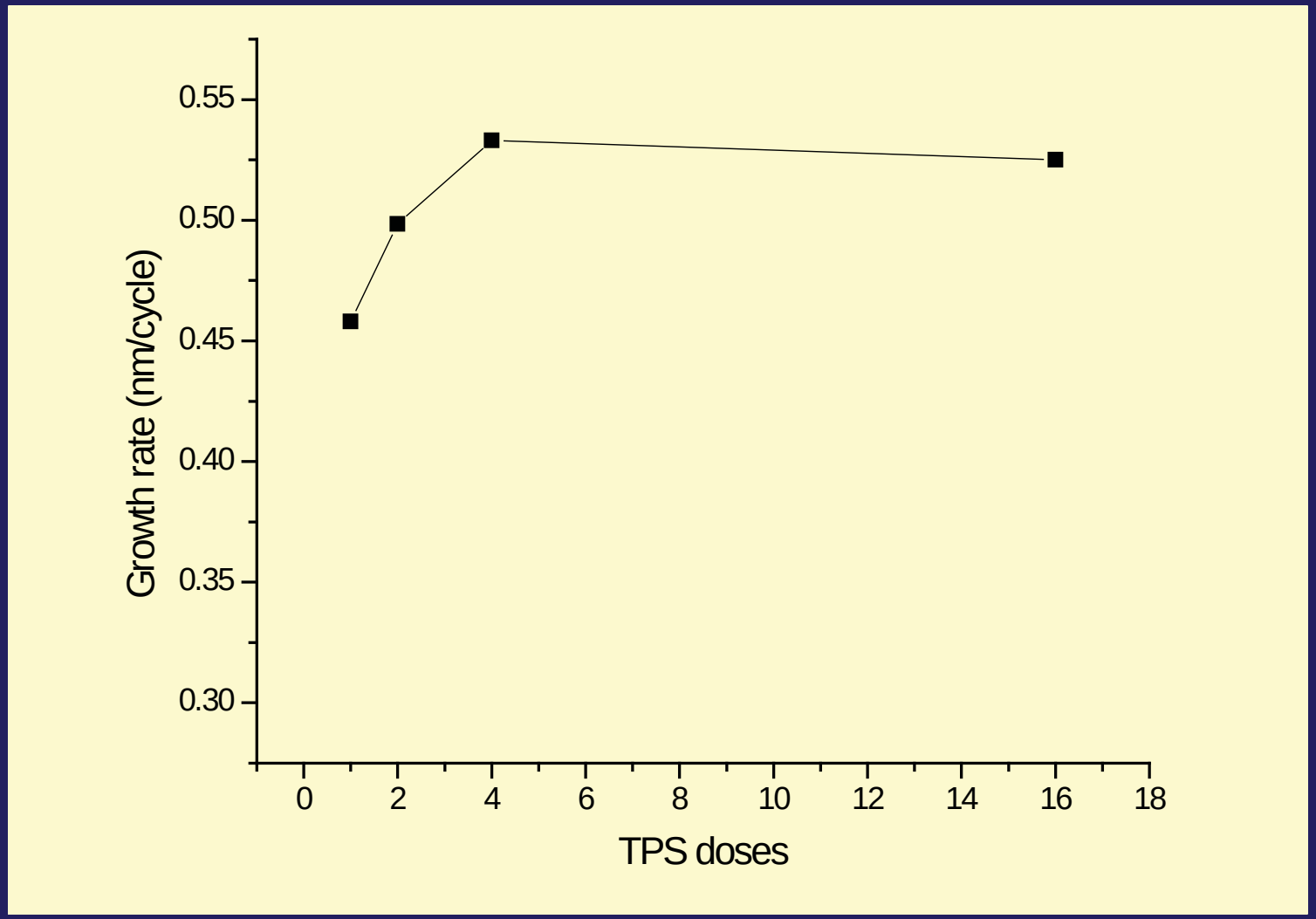
Cycle times (s): 1/30/4/30
(Mn(amd)/purge/TPS/purge)

growth per cycle = 0.43 nm

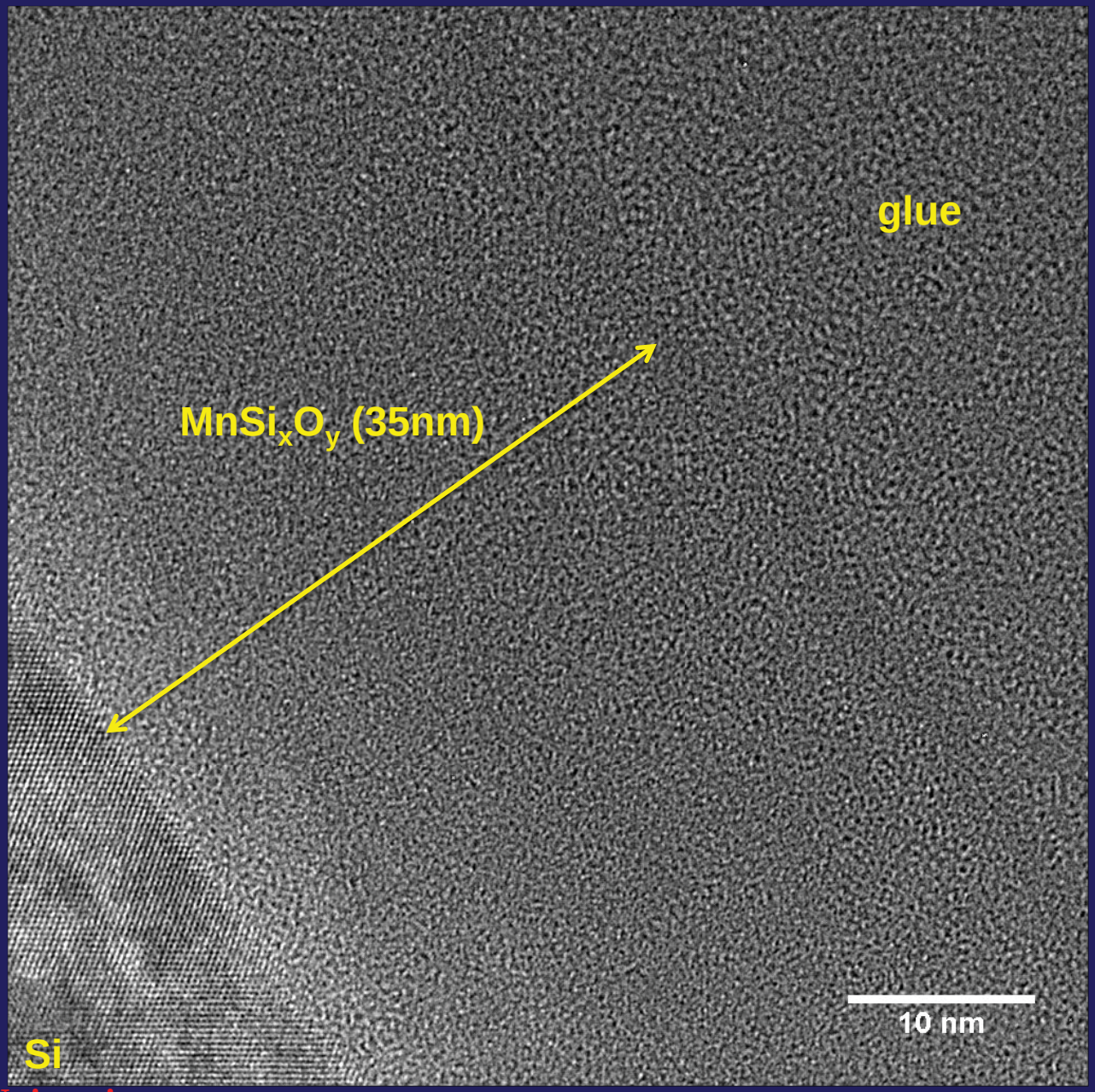


High growth per cycle due to a catalytic mechanism similar to that of aluminum-catalyzed silica: Dennis Hausmann, Jill Becker, Shenglong Wang, Roy G. Gordon, Science 298, 402 (2002)

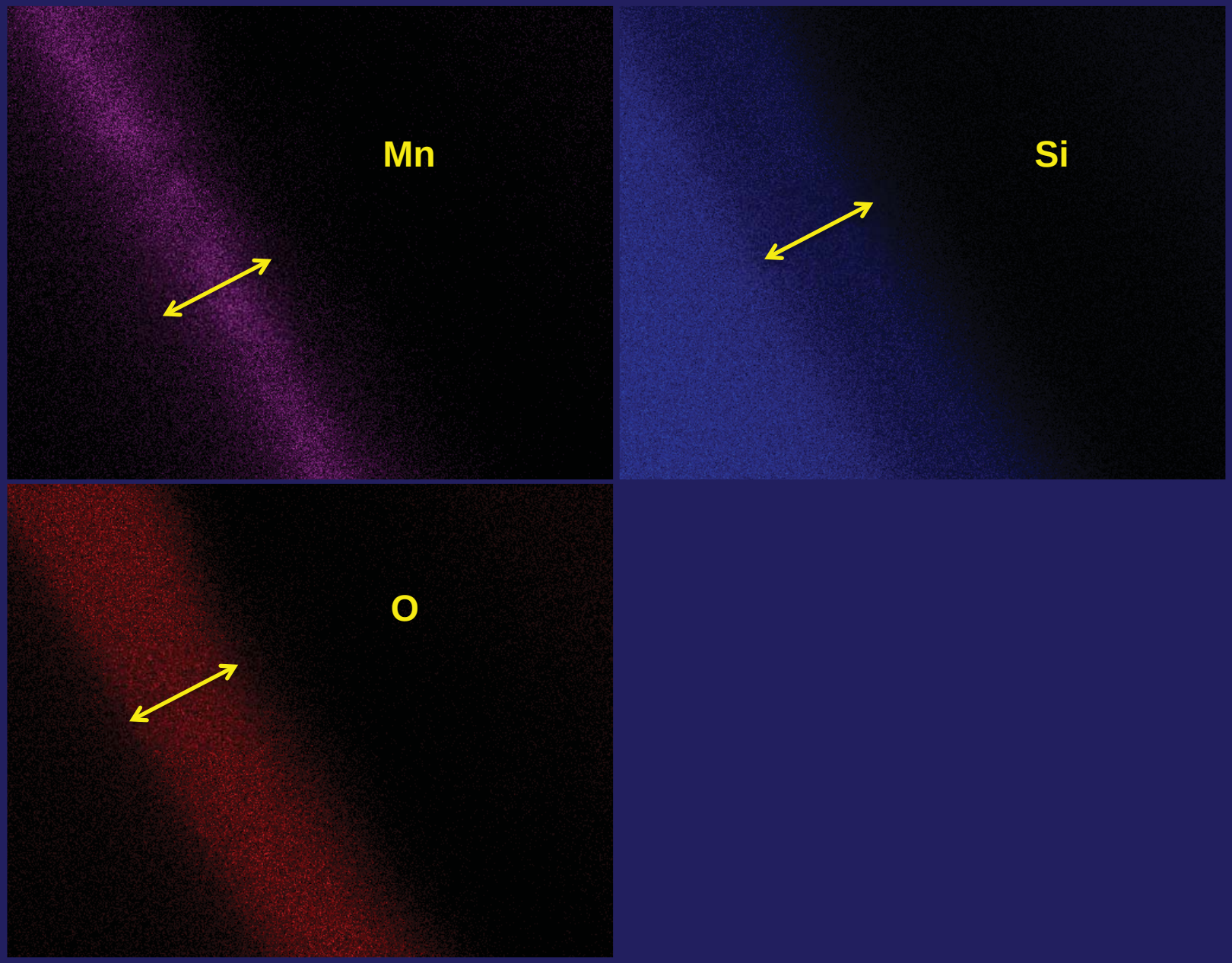
Saturation Curve for $MnSi_xO_y$ vs. Silicate Precursor



TEM => Amorphous Structure



STEM EDX Mapping of Elements



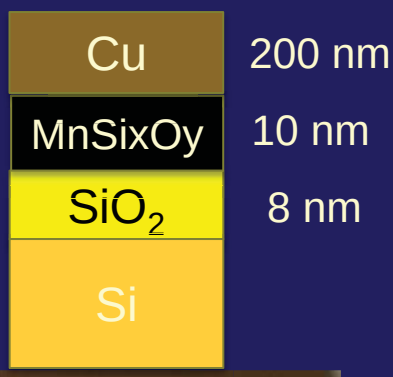
Composition by Rutherford Backscattering Spectroscopy

Cycles	Mn 10^{15}at/cm^2	Si 10^{15}at/cm^2	O 10^{15}at/cm^2	Mn:Si:O
10	2.32	6.2	24	**1 : 2.7 : 10**
20	5.56	15	47	**1 : 2.7 : 8**
50	15.4	41	117	**1 : 2.7 : 7.6**

Stoichiometry ~ $MnSi_{2.7}O_{7.6}$ so Mn is oxidized to Mn^{4+}

Cu diffusion test

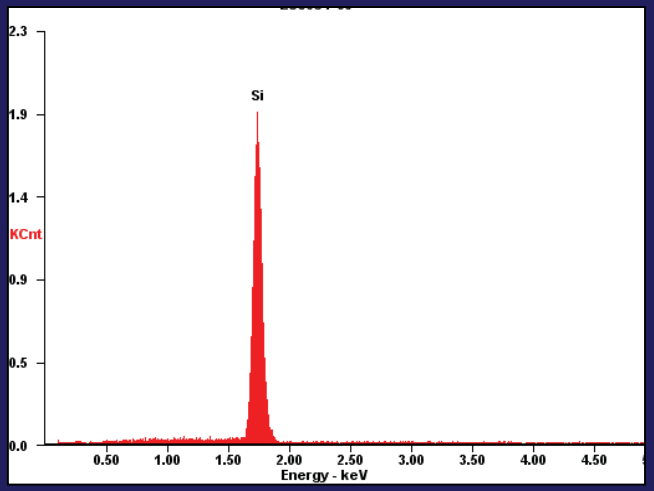
anneal samples in N_2 for 1h at 450 C, use Ni etchant to remove Cu film, then EDX

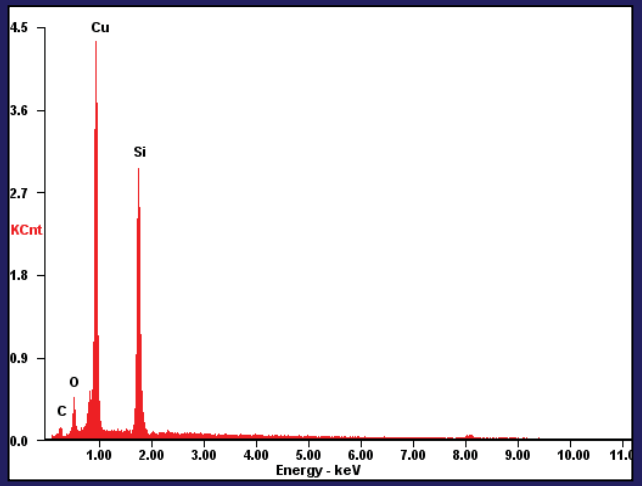


200 nm
10 nm
8 nm

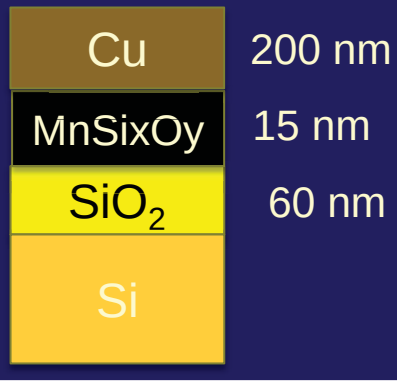
200 nm
8 nm

visible appearance





CV tests after electric field at room temperature



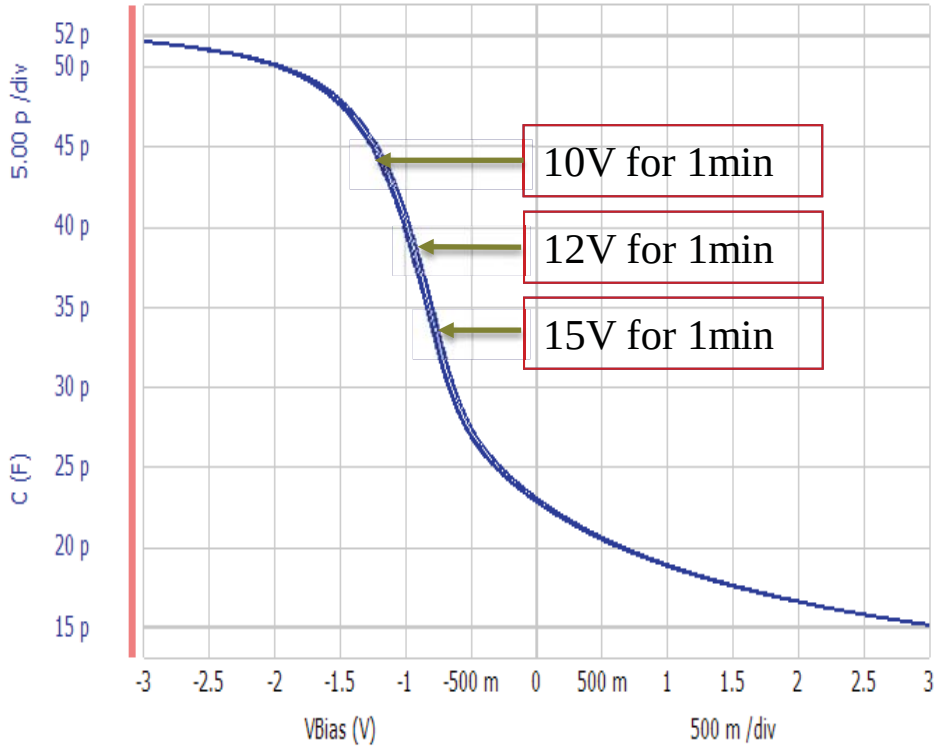
200 nm

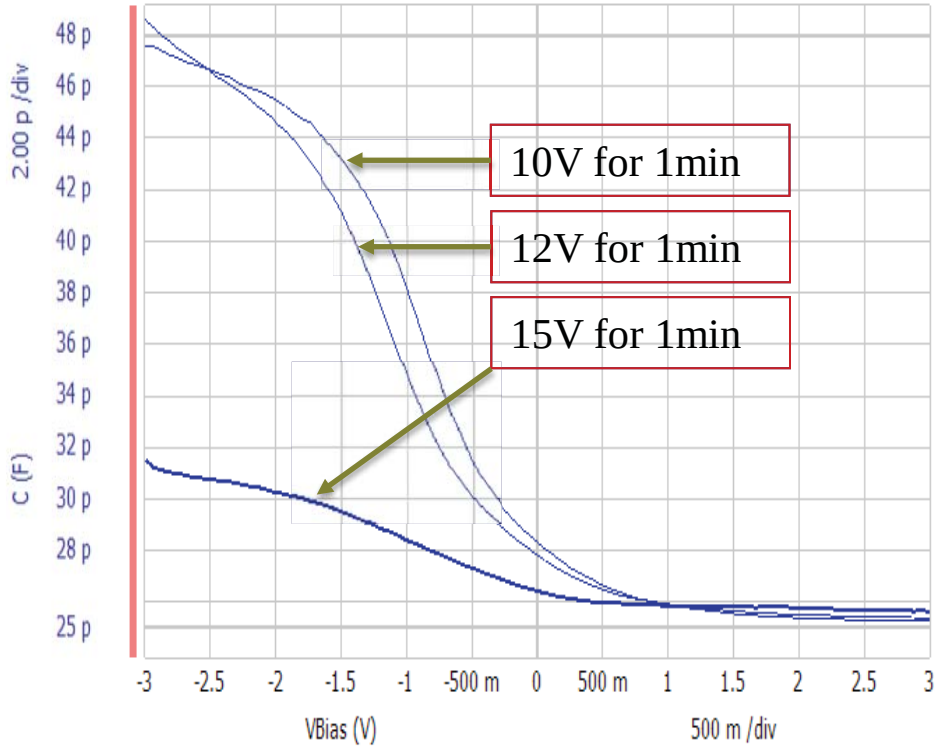
15 nm

60 nm

200 nm

60 nm





Effectiveness of $MnSi_xO_y$ as a Cu Diffusion Barrier

Composition	Structure	Cu Barrier	Diffusion Pathway
SiO_2	amorphous	no	open tetrahedral network
$MnSi_{2.7}O_{7.6}$	amorphous	yes	paths blocked by Mn ions
MnO	polycrystalline	no	grain boundaries

Acknowledgements

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